SINTERING SPECIFICS OF CORUNDUM CERAMICS MODIFIED WITH EUTECTIC ADDITIVES

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Methods used for analyzing the regularities of thermally activated processes are considered. It is demonstrated that the most informative and reliable are nonisothermal methods. Taking the example of alumina materials modified by eutectic additives of systems $MnO – Al_2O_3 – SiO_2$, $CaO – ZnO – Al_2O_3 – SiO_2$, and $ZnO – TiO_2$, it is established that their consolidation kinetics obeys a first-order formal kinetic equation. The apparent energy of sintering activation is determined The calculation of sintering regularities by nonisothermal kinetic method makes it possible to design schedules for heat treatment of articles.

Physicochemical processes that are activated with increasing temperature are studied using two groups of methods. The first group includes isothermal methods when the kinetic parameters of the sintering process are determined by multiple firing of samples within a certain temperature interval with varying exposures at each temperature [1]. These methods, as a rule, are labor-consuming, and to improve their reliability the number of samples has to increase manyfold. Furthermore, purely isothermal conditions are usually difficult to achieve, since protracted heating of samples to a required temperature is accompanied by significant shrinkage, which perceptibly distorts the results. Therefore, researchers now extensively use nonisothermal methods, where the temperature of a sample varies with time according to a specified law [2]. These methods are most informative, allow for covering a wide range of parameter variations, and ensure a high reliability of results.

However, any kinetic study is based on two main principles. The first principle is that each stage of a physicochemical process, such as diffusion, formation or breaking of chemical bonds, etc. is accompanied by the formation of an activated complex whose formation energy in the direction of the reaction considered is maximal. This means that of all possible directions of a chemical reaction, the one that has the minimal energy barrier is actually implemented. On the other hand, the speed of a multistage process consisting of a series of consecutive stages depends on the speed of its slowest stage.

An activated complex is always in equilibrium with the reactants, even when the time of its existence is negligibly small. Furthermore, the rate of disintegration of an activated complex is a universal constant equal to $KT/\bar{h}$ (K is the Boltzmann constant, $\bar{h}$ is Planck's constant).

It is accepted in the contemporary theory of chemical kinetics that a process in time can be described by the equation

$$\frac{d\alpha}{d\tau} = k_0 \exp\left(-\frac{E}{RT}\right) F(\alpha), \qquad (1)$$

where α is the degree of transformation of the reactants in time τ; $\frac{d\alpha}{d\tau}$ is the rate of the process studied; k_0 is the pre-exponential factor; E is the apparent energy of the process activation; R is the universal gas constant; $F(\alpha)$ is a function depending on the process mechanism, i.e., the kinetic model of the process.

It should be noted that the parameter α can be taken as air or fire shrinkage, water absorption, porosity, density, viscosity, or some other parameters of the system that characterize the process. In our case we have selected relative linear shrinkage as this parameter, i.e., the ratio of the current shrinkage of a sample to its maximum possible value.

Based on the law of mass, we write

$$\frac{d\alpha}{d\tau} = -\frac{d(1-\alpha)}{d\tau} = k(1-\alpha)^n, \qquad (2)$$

where $k = k_0 \exp\left(-\frac{E}{RT}\right)$.

In some cases when studying sintering kinetics by the nonisothermal method it is convenient instead of linear shrinkage α to use the dimensionless parameter z related to α as follows: $z = 1 - \alpha$.

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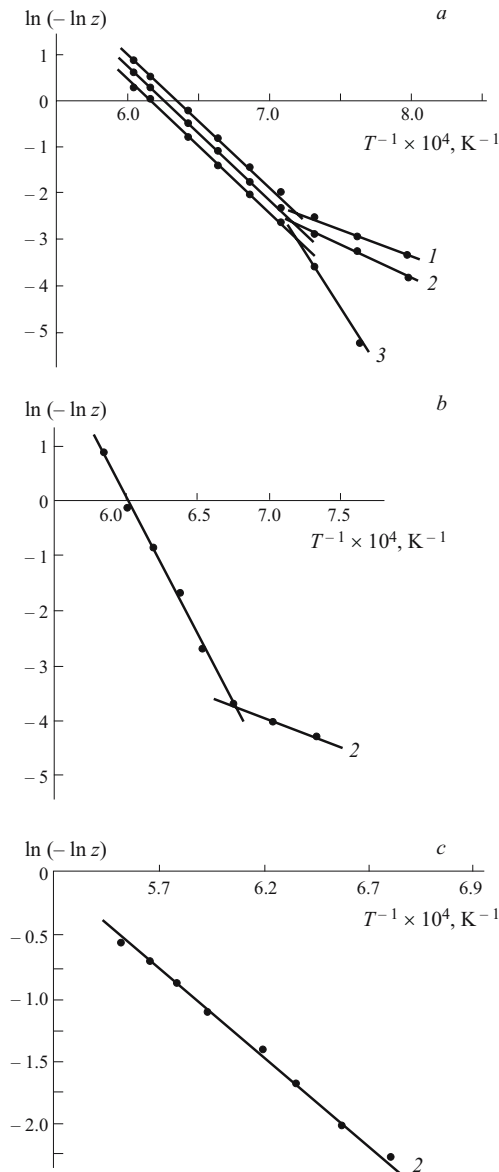**Fig. 1.** Determination of apparent activation energy of sintering for samples containing additives of systems $MnO - Al_2O_3 - SiO_2$ (a), $CaO - ZnO - Al_2O_3 - SiO_2$ (b), and $ZnO - TiO_2$ (c): 1, 2, 3) molding pressure of 50, 100, and 400 MPa, respectively.

Then based on expression (2) we obtain transformed Eq. (1):

$$\left.\begin{array}{l} \dfrac{dz}{d\tau} = -kz^n; \\[2mm] F(z) = -z^n. \end{array}\right\} \tag{3}$$

The value n in formulas (3), analogously to the formal kinetics of reactions in gases and liquids, can be regarded as the order of the sintering process.

Equations (3) characterize physicochemical processes controlled by a single mechanism. A change of this mechanism will also change the kinetic parameters (k_0, E, n),

which can be clearly registered in nonisothermal analysis. Consequently, such analysis makes it possible to identify the temperature boundaries of the prevalence of a particular mechanism.

Let us assume that the sintering process is a reaction whose formal order is equal to unity. Then by integrating Eq. (3) in the limits from $z_0 = 1$ to z and from $\tau_0 = 0$ to τ we have

$$\ln(-\ln z) = \ln(k_0 \tau) - \frac{E}{RT}. \tag{4}$$

Considering that $\tau \sim 1/v$ (v is the furnace heating rate) and substituting k_0' for k_0 in expression (4) we obtain

$$\ln(-\ln z) = \ln\left(\frac{k_0'}{v}\right) - \frac{E}{RT}. \tag{5}$$

Thus, based on Eq. (5) it becomes possible to determine E by the graphical method.

To analyze the applicability of the formally first-order kinetic equation to the regularities of the consolidation of materials containing additives that form a eutectic composition in sintering, we have analyzed mixtures with modifiers represented by the eutectics of the systems $MnO - Al_2O_3 - SiO_2$, $ZnO - TiO_2$, and $CaO - ZnO - Al_2O_3 - SiO_2$. These additives were introduced in aluminum oxide synthesized from industrial hydroxide by its preliminary milling in a magnesium salt solution (0.25% MgO, here and elsewhere wt.%, based on calcined hydroxide), calcination at 1350°C, and a second milling. The quantity of the additives introduced was 4% $MnO - Al_2O_3 - SiO_2$ and $CaO - ZnO - Al_2O_3 - SiO_2$ and 1% $ZnO - TiO_2$.

To synthesize the sintering additives, initial mixtures were charged into Teflon drums of a vibrating mill, mixed with distilled waster, and milled for 3 h using corundum balls.

The initial component mixtures for each additive were calcined at a temperature of 1000°C and the mixture for the system $MnO - Al_2O_3 - SiO_2$ was calcined at 700°C. The exposure at the maximum temperature lasted 3 h, and the furnace heating rate was 1.5 K/min. Heat-treated materials were subjected to moist milling in the same conditions as before the synthesis.

Samples (shapes as bars of size $40 \times 6 \times 4$ mm) were molded by two-sided uniaxial semidry molding at molding pressures of 50 and 100 MPa and also by hydrostatic molding at a pressure of 400 MPa. In the latter case bars of size $40 \times 6 \times 4$ mm were first produced by semidry molding from the molding powder, then placed in an elastic latex shell, dried, and compressed at the specified pressure. Firing was carried out in air at the heating rate of 3 K/min in the temperature interval of 1100 – 1550°C.

The results of the experiments are shown in Fig. 1. It can be seen that the consolidation regularities for mixtures con-

taining eutectic additives can be satisfactorily described by a first-order equation of formal kinetics. The correlation coefficient in all cases considered is at least 0.95. It is important that in the context of formal kinetics the order of the reaction is identical both in the temperature range where the process proceeds with the participation of a liquid phase and in the range where the liquid phase is absent. These processes have different values of apparent activation energy.

Thus, the sintering of ceramics with an additive of the $MnO - Al_2O_3 - SiO_2$ system occurs in two stages. The activation energy of the first stage E_1 varies within wide limits (from 150 to 360 kJ/mole) depending on molding pressure. Therefore, the process kinetics at this stage is determined by the contact geometry. An increase in molding pressure produces a denser packing of particles, which hampers their motion at the initial phase of sintering and is responsible for the higher apparent activation energy.

The process activation energy at the second stage E_2 does not depend on the geometry of contacts between the particles and is equal to 228 ± 20 kJ/mole for the pressure interval considered. The change of in prevailing mechanism occurs at a temperature of approximately 1140°C. The prevailing mechanism above the specified temperature is the dissolution of the high-melting component and its subsequent crystallization.

The analysis of the behavior of the additive mixture in a derivatograph furnace indicates that the thermogram has an endothermic peak in the temperature interval of $1135 - 1165 - 1215$°C related to the melting of the eutectic.

The model experiment of melting a tablet-shaped additive placed on a substrate of the same aluminum oxide that was used to mold samples demonstrated that melting occurs at a temperature of 1130°C.

The experiments performed suggest that the prevailing sintering mechanism changes at the moment of emergence of a liquid phase in the system.

Based on microscopic analysis data, the quantity of the melt in the system under sintering grows insignificantly and amounts to $7 - 8$ vol.% at the final stage of the process. This suggests that the composition of the liquid in firing does not deviate from the eutectic. Consequently, it can be stated that the phases of the sintering additive are crystallized in the cooling of the system at the eutectic melting temperature.

The composition containing a eutectic additive of the $CaO - ZnO - Al_2O_3 - SiO_2$ system behaves in the similar way. Sintering occurs in two stages (Fig. 1): $E_1 = 132$ kJ/mole, $E_2 = 367$ kJ/mole. The prevailing mechanism changes at a temperature of about 1200°C, which is close to the eutectic melting point.

At first glance, the sintering regularities of the composition containing a eutectic additive of the $ZnO - TiO_2$ system are somewhat different. In contrast to the above described compositions, there are no bends on the curve presented in the linear form (Fig. 1). This could point to a unique sintering mechanism for the whole temperature range consi-

dered. However, such interpretation is erroneous. Apparently the activation energy of the stage with the participation of the liquid phase coincides with the activation energy of the process prior to the modifying additive melting point (in the considered case this is approximately 120 kJ/mole); therefore, no bends are registered on the curve.

After determining the main kinetic parameters, the issue is their possible application in research and industrial practice, namely, their application in developing rational firing procedures, which is discussed in a number of studies [3, 4].

Corresponding calculations can be performed based on the results of the nonisothermal studies of the sintering process. Thus, from Eqs. (2) and (3) it follows that

$$T = -\frac{E}{R \ln\left(\dfrac{k_0 F(z)}{dz / d\tau}\right)}. \tag{6}$$

Assuming that $\dfrac{dz}{d\tau} = $ const and using expression (6) we can calculate the necessary firing schedule. Taking into account that $F(z)$ can be determined from formula (3) $z_0 \geq z \geq z_{max}$ and $T_{max} \geq T \geq T_0$, we have

$$T = \frac{\dfrac{E}{nR}}{\dfrac{E}{nRT_{max}} + \ln\left[\dfrac{z_0}{z_{max}} - k_0 \exp\left(-\dfrac{E}{RT_{max}}\right) z_{max}^{n-1}\tau\right]}. \tag{7}$$

Relation [7] makes it possible to obtain the temperature regime in explicit form, in which uniform and as fast as possible sintering can be achieved. For our case ($n = 1$),

$$T = \frac{E / R}{\dfrac{E}{RT_{max}} + \ln\left[\left(z_0 - k_0 \exp\left(-\dfrac{E}{RT_{max}}\right)\tau\right)\dfrac{1}{z_{max}}\right]}. \tag{8}$$

Thus, calculation of the regularities of sintering by nonisothermal kinetic methods is essential for industrial practice as well, since on this basis it is possible to develop schedules for heat treatment which in industrial conditions, and often in laboratories as well, proceeds in a nonstationary temperature field.

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